ESTERIFICATION OF HIGHLY ACIFIED USING WASTE COOKING OIL USING IONIC LIQUID SUPPORTED BY DIVINYL BENZENE AS CATALYST

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ABSTRACT

The depletion of natural resources around the world led the researcher looking forward for alternatives renewable sources. Biodiesel has been chosen as a good alternative to replace the petroleum. Many researchers used virgin oil as the raw material to produce biodiesel. However, virgin oil is quite expensive and increased the competition between food and fuels. Therefore, waste cooking oil has been chosen as the alternative feedstock used in this research compared to edible oil. On the other hand, acidified oil such as waste cooking oil and animal fats was found to gives a good conversion of triglycerides via the two step esterification- transesterification reaction. Esterification process is needed in the pretreatment of acidified oil to reduce the FFA content in the feedstock itself before it could be proceed with transesterification. The objective of this study is to synthesize and characterize the triethylammonium hydrogen sulphate ionic liquid and supported triethylammonium hydrogen sulphate ionic liquid and to conduct the catalytic esterification reaction using both type of catalyst. The catalyst was characterized using NMR, FTIR, SEM and BET. The NMR spectrum are as ^{1}HNMR, (500MHz, DMSO) (ppm): ∂ 1.19 (triplet, 9h) ∂ 3.09 (multiplet, 6H) ∂ 6.95 (singlet, 1H) ∂ 9.01 (singlet, 1H). The IR spectrum of ionic liquid are sulphonic acid at 1061 and 1149 cm^{-1}, including C-C (1233 cm^{-1}), Ar-H (2506 cm^{-1}) and OH (3037 cm^{-1}). The IR spectrum for supported ionic liquid are 1101 and 990 cm^{-1} for sulphonic group, C-C (1168 cm^{-1}), Ar-H (2924 cm^{-1}) and OH (3445 cm^{-1}). The supported ionic liquid has surface area of 22.34 m^2 /g and the pore volume is 0.0327cm^3/g. The pore size of supported ionic liquid is 2.6 nm. The esterification of highly acidified oil is conducted at temperature of 60^0C, 2.5 wt % of catalyst and the molar ratio of methanol to waste cooking oil of 18:1. As a conclusion, both catalysts are not able to reduce free fatty acid and have zero conversion. This is due to unsuitable ratio of methanol to oil and temperature of the reaction.

ABSTRAK

Kepupusan sumber asli di seluruh dunia menyebabkan penyelidik mencari sumber baru sebagai alternatif tenaga guna pakai. Biodiesel adalah salah satu alternatif untuk mengantikan petroleum. Kebanyakan penyelidik mengunakan minyak kelapa dara sebagai bahan asas untuk menghasilkan biodiesel. Walaubagaimanapun, minyak kelapa dara adalah mahal dan meningkatkan pertandingan makanan dan minyak. Oleh itu, minyak masak dipilih sebagai alternatif bahan mentah untuk kajian ini. Di samping itu, minyak asid seperti minyak buangan dan lemak haiwan meberikan pertukaran triglycerine yang bagus melalui dua tahap esterificasi–tansesterifikasi tindak balas. Proses pengesteran diperlukan dalam prarawatan minyak berasid untuk mengurangkan kandungan FFA dalam bahan mentah itu sendiri sebelum ia boleh meneruskan transesterifikasi. Objektif kajian ini adalah untuk mensintesis dan mencirikan cecair ionik triethylammonium hidrogen sulfat dan disokong triethylammonium hidrogen cecair ionik sulfat dan untuk menjalankan tindak balas pengesteran pemangkin menggunakan kedua-dua jenis pemangkin. Pemangkin dianalisa mengunakan NMR, FTIR, SEM dan BET. NMR spectra menunjukan ^{1}HNMR, (500MHz, DMSO) (ppm): ∂ 1.19 (triplet, 9h) ∂ 3.09 (multiplet, 6H) ∂ 6.95 (singlet, 1H) ∂ 9.01 (singlet, 1H). IR spectra cecair ionik adalah asid sulphonic pada 1061 and 1149 cm^{-1}, termasuk C-C (1233 cm^{-1}), Ar-H (2506 cm^{-1}) dan OH (3037 cm^{-1}). IR spectra untuk sokongan cecair ionik adalah 1101 dan 990 cm^{-1} untuk asid sulfonic, C-C (1168 cm^{-1}), Ar-H (2924 cm^{-1}) dan OH (3445 cm^{-1}). Sokongan cecair ionik mempunyai keluasan permukaan pada 22.34 m^2/ g dan isipadu pada 0.0327cm^3/ g. Saiz sokongan ionik adalah pada 2.6 nm. Esterifikasi minyak asid dijalankan pada suhu 60^0C, 2.5wt % pemangkin dan nisbah metanol kepada minyak masak adalah 18:1. Sebagai konklusi, kedua-dua pemangkin tidak dapat mengurangkan asid lemak bebas dan tidak mempunyai pertukaran. Ini disebabkan oleh nisbah minyak kepada methanol dan suhu yang tidak sesuai untuk tindak balas.

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LIST OF ABBREVIATIONS

DVB	Divinyl Benzene
IL	Ionic Liquid
FFA	Free Fatty Acid
KOH	Potassium Hydroxide
FTIR	Fourier Transform Infrared spectroscopy
NaOH	Sodium Hydroxide
NMR	Nuclear Magnetic Resonance
SIL	Supported Ionic Liquid
TGA	Thermal Gravimetric Analysis
WCO	Waste Cooking Oil

1 INTRODUCTION

1.1 Motivation and statement of problem

Currently, our energy sectors depend on fuels derived from fossil resources. Thus, there is a concern about the current status of world's oil reserves and increasing environmental impacts of these fuels. There is a great expectation for alternative sources of energy from clean and renewable sources such as biodiesel.

Biodiesel is a mixture of a mono-alkyl esters of long-chain fatty acids that is formed from renewable raw materials like vegetable oil, animal fats and waste cooking oil (Adewuy et al., 2012; Deeba et al., 2012; Zhang et al., 2013). The benefits using biodiesel are renewable, green fuel, biodegradable, non-toxic, less sulphur content and high cetane number. There are different type of sources to produce biodiesel such as jatropha oil, waste cooking oil, rapeseeds oil, karanja oil, corn oil and algae. The raw material designed for biodiesel production has different content of the free fatty acid (FFA). Therefore, the process used is different according to their type of the raw material.

Biodiesel research has gain interest nowadays and increased publication by each year due to reducing of petroleum reserves. The main feedstock for biodiesel is edible oil and these create the food versus fuel issues. This phenomena contributes to the rise in cost of food items around the world. Besides, the production of waste cooking oil has increased due to the increasing of food consumption in restaurant. Therefore, WCO has become a viable alternative to replace edible oil as the feedstock for biodiesel production. In addition, the usage of WCO as the feedstock could reduce the competiton between food and fuel supply.

Generally, biodiesel can be produced using different types of processes such as direct blending, thermal cracking, microemulsion, transestrification and esterification. Direct blending, thermal cracking and microemulsion result in several disadvantages such as pollution, incomplete combustion and produced side products. The most common method used for converting oil to biodiesel is the transesterification but the main drawback is on the production of soap when the feedstock with high FFA is used. Furthermore, the reaction rate is slower. Thus, esterification is the best alternative

process compared to transesterification because can treat high FFA feedstock. Esterification is processes which form ester and water with the aid of catalyst.

Most of esterification was catalyzed using acid homogeneous catalyst. Current researches are focusing on the usage of heterogeneous catalyst as it improved the product selectivity and easy catalyst separation from reaction mixture, reducing process stages and wastes. One of the heterogeneous catalyst that gain tremendous intense is the ionic liquid (IL). IL is a group of salt with a wide range of temperature range for the liquid phase. The properties of IL depend on the ionic structure of anion and cation such as non-flammability, high thermal conductivity and high density (Wu et al., 2001). The advantages of having IL as the catalyst are due to its low cost and little amount of energy used. However, IL has some disadvantage such as catalyst lost during the process, limited the solubility's with organic molecules and difficult in the purification process (Liang, 2013). Thus, the immobilization IL is one of the alternatives to overcome those problems. Different type of supported have been done by using porous silica, polystyrene, silica and divinyl benzene. Divinyl benzene shows a good behaviour and reduced the cost.

Thus, this research will focus on the usage of supported ionic liquid by divinyl benzene as the catalyst for esterification of free fatty acid in acidified oil. Simulated acidified oil will be used as a feedstock and will be pretreatment the oil using supported IL.

1.2 Objectives

The purpose of this research was to investigate the performance of FFA esterification in highly acidified oil using supported triethylammonium hydrogen sulphate ionic liquid.

1.3 Scope of this research

The scopes of this research work are:

i) To synthesize and characterize the triethylammonium hydrogen sulphate ionic liquid.

ii) To synthesize and characterize the supported triethylammonium hydrogen sulphate ionic liquid

iii) To conduct a catalytic activity test for FFA esterification using ionic liquid and supported triethylammonium hydrogen sulphate ionic liquid as catalyst.

1.4 Main contribution of this work

This work is contributions towards economy, nation and environment. In term of economy, this experiment gives a lot of benefit like the process and behaviour of the catalyst. In term of environment, this catalyst will act as the green solvent and can reduce the waste form from the experiment.

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a description of the esterification process, feedstock and type of catalyst. This chapter also provides a brief discussion of the process available for esterification process. A summary of the previous experimental work on esterification process and feedstock used in order to choose which process is suitable for different type of feedstock.

Chapter 3 gives a review on the method of FFA esterification process. A review on the characterization of the catalyst using Fourier Transform Infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Brunauer- Emmett- Teller (BET), Nuclear and Magnetic Resonance (NMR). The method of ASTM D974 will be used to test the acid number of FFA in waste cooking oil.

Chapter 4 is to discuss about the result obtained in detailed. The catalyst will be characterized using FTIR, SEM, BET and NMR to study the chemical structure, morphology surface and chemical composition of IL and supported IL.

Chapter 5 is to conclude about the catalyst that been synthesized and characterized. The suggestion to improve the research work will be briefly discuss.

2 LITERATURE REVIEW

2.1 Energy

Energy is widely used in many sectors such as transportation, industrial zone, residential, and agricultural sectors. There are many forms of energy which are chemical energy, electrical energy, heat or thermal energy, light energy, mechanical energy, nuclear energy, kinetic and potential energy. There are two main different sources of energy which is renewable energy and non-renewable energy. Non-renewable energy is the sources that will run out or will not be fill again for thousands or even millions of years. The examples of non-renewable energy are fossil fuels, coal and natural gaseous. The reduction of fossil fuel was due to high demands in industrial situation as well as domestics sector and causes the pollution issues. Energy is unsuitable due to equity issues like environmental and economic. In environment aspect it may harms the green house which cans thinner the ozone layer. Furthermore it can lead to pollution which increase a global temperature and also increase in sea levels. Besides that, the effect on the economic sector is the energy depends on the sustainability of economic. This is because most of the industries used energy to produce product. Thus renewable energy is the beginning steps to reducing pollution. Renewable energy is the energy which can be obtained from natural resources which can be constantly provided. The type of renewable energy are solar, wind, geothermal, biomass and hydropower energy. The renewable source has become more popular due to the decreases of petroleum resources and environment and exhaust of green layer in the atmosphere because of the usage of petroleum. Biodiesel is comprises of monoalkyl esters of long chain fatty acids that derived from renewable sources. Biodiesel is the one of the renewable energy. The advantages of biodiesel as a fuel are it's able to reduce carbon dioxide, hydro carbon and carbon monoxides. It's also has non-toxic character and had a better quality of exhaust gases. The disadvantages of using biodiesel are practically economically is due to its higher price.

2.2 Process for biodiesel production

2.2.1 Introduction

Biodiesel is described as the mono-alkyl esters of vegetable oils or animal fats. It was produced from a process known as transesterification where triglycerides are reacted with alcohol in the presence of acid or basic catalyst. Biodiesel is a very environmentally friendly energy source and biodegerable. There are a few types of biodiesel production route such as direct blending, pyrolysis, microemulsion, esterification and transesterification. Direct blending is a process of direct usage of oil to be blend with diesel. The advantage of direct blending is it improved the viscosity of oil. Pyrolysis is a thermal cracking process the uses the heat at high temperature to change the chemical structure of oil to form biodiesel with the aid of catalyst. The benefits of pyrolysis are effective and simple process. However, pyrolysis is difficult to characterize, wasteless and causes to pollution. Microemulsion is defined as the dispersion of oil in water in oil with the aid of surfactant. The application of microemulsions can solve the problem of high viscosity of vegetable oils (Fukuda et al., 2001). Microemulsion can improved the spray characterization. The disadvantages of microemulsion is due the to incomplete combustion cause by a low cetane number. Furthermore, the process is complicated to operate and produce side products. Transesterification is known as alcoholysis. This process is the reaction involving between a fat or oils with alcohols to yield ester and glycerol. Examples of alcohol used in this process are methanol, ethanol, propanol and butanol. These processes consume shorter time duration but produced soap during the reaction.

2.3 Feedstock

Most of the biodiesel feedstock is usually comes from renewable sources and easily available. The examples of the feedstock used are edible oil, non-edible oil, waste cooking oil, animal fats and algae.

2.3.1 Edible oil

Edible oil is the vegetable oil that used for human consumption. The examples of edible oil are rapeseed oil, soybean oil, camelina sativa oil, sunflower and palm. Difference types of vegetable oil have different composition when they are thermally decomposed. The benefit of using edible oil as the feedstock is because it is easily available and can be regenerated. The disadvantages of using edible oil are due to its high viscosity, low

volatility and costly. Different countries used different types of vegetable oil as biodiesel feedstock for example are European countries used rapeseeds oil, United State used soybean oil, South Africa used sunflower oil, and Philippines used coconut oil. Berrios et al. (2007) studied on kinetic of the esterification of FFA in sunflower oil. They concluded that using a 5% sulphuric acid concentration can be effectively removed the FFA content of the feedstock. Other researcher also found that the reaction of oleic acid with methanol in the presence of sunflower oil using ferric sulfate supported on silica as a catalyst are able to obtain 96.9% conversion of oleic acid (Dokic et al., 2012). Xie et al. (2013) found that the methyl ester conversion is about 96.7 % using soybean oil and phenylsulfonic acid functionalized SBA-15 silicain as the feedstock and catalyst. Jeong and Park, (2006) studied on the efficiency of batch production of biodiesel fuel from rapeseed oil. They studies on the performance of single and multiple stage of transesterification. They found that two stage transesterification obtain higher conversion compared to one stage because two stage is more efficient in biodiesel production. Besides that, Xie et al. (2012) studied on the transesterification of soybean oil using silica-supported tin oxides SnO_2/SiO_2 as catalysts. The maximum activity is obtain at 8 wt % tin (Sn) loading which can catalyze the transesterification reaction of soybean oil with large amount of FFA and achieved about 81.7% conversion of soybean oil.

2.3.2 Non edible oil

Non edible oil is defined as waste edible vegetable oil and not suitable for human consumption due to the toxic content (Bouaid et al., 2012). The examples of non-edible oil are mahua, jatropha, tobacco seed and rubber plant. Godugula and Srinivas. (2012) studied the two stage esterification- tranesterification using Pongamia pinnata as the feedstock and obtain 91% conversion of FFA. Bala et al.(2012) also studied FFA esterification using Pongamia oil with different types of divinyl benzene-styrene copolymer resins such as Amberlite IR 120 H and Amberjet 1200 H. Highest conversion was archieved using Amberlite IR 120 H, astrongly acidic ion exchange resin which yield 96% of FFA conversion. The maximum yield of methyl esters obtain from rubber seed oil involves with two steps pre-treatment is about 85% conversion (Thangaraj and Paul Raj, 2014). Jatropha curcas oil shows the highest reaction conversion of 99.7% when using KOH as the catalyst (Syam et al., 2011). Gunawan et al. (2014) studied the two-step process of esterification-transesterification analyse using

Xylacarpusmoluccenis seed oil and palm oil. The study showed that the biodiesel produced from X. moluccensis seed oil has better cold flow properties compared to palm oil. The advantages of using non edible oil are it is carbon–neutral, reduces waste and improve the resource efficiency. However, the production of biodiesel from non-edible oil is slightly expensive due to the requirement of two-stage reaction to neutralize the FFA content.

2.3.3 Waste cooking oil

Waste cooking oil (WCO) is a very attractive feedstock for biodiesel production. It is cheaper compared to edible oil and avoids the issues of food versus fuel. The sources of WCO are usually obtained from restaurant and markets. WCO contain of undesirable compounds such as polymers, free fatty acid (FFA), and many other chemicals. Chakraborty and Das. (2012) has done research on the optimization of biodiesel synthesis using waste frying soybean oil supported by Nickel catalyst. They obtain 98.4% yield of biodiesel and shows that acid catalyst able to convert high acid value into biodiesel. Felizardo et al. (2006) studied on the production of biodiesel from waste frying oil using methanol and sodium hydroxide as catalyst. An increase in the amount of methanol can easily purify of the methyl esters phase and obtain highest conversion. According to Boffito et al. (2013) blending between waste cooking oil and rapeseed oil can reduce the viscosity of oil and obtain higher conversion of biodiesel. The advantages of WCO are one of the economical sources for biodiesel production, gives better engine performance and less emission and low cost compared to edible oil.

2.3.4 Animal fats

Examples of the animal fats that make to produce biodiesel are tallow, lard and poultry fat. These alternative resources of biodiesel feedstock have several advantages such as carbon-neutral feedstock, reduces waste, improve the resource efficiency, high cetane number and non-corrosive. Bhatti et al. (2008) studied on the biodiesel production from waste tallow. They concluded that using acid catalyst give higher yield compared to base catalyst. Shi et al. (2013) found that the free fatty acids (FFAs) in the chicken oil were changed to methyl esters by esterification. They obtain 98.1% under the optimum conditions An esterification process is recommended to lower FFA content in waste animal fat using solid acid ion exchange resins as catalysts and the FFA conversion was found to be greater 90% (Bianchi et al., 2009).

2.3.5 Algae

Algae are one of the feedstock used to produce biodiesel. It is known as a rapid growing plants and one of the biomass source. Algae consist of protein, carbohydrates, lipids and nucleic acids. It have four main classes of algae which are diatoms (bacillariophyceae), green algae (chlorophyceae), blue green algae (cyanophyceae), and golden brown algae (chrysophyceae). The most encourage division used to produce biodiesel is diatoms and secondary algae. Algae have two main population which are filamentous and phytoplankton. The researcher had found that there are three methods to biodiesel produce using algae. The first method is a two step method where algae was extracted using organic solvent and then converted to biodiesel using an acid catalyst (Krohn et al., 2011; Nagle and Lemke, 1990), a base (Umdu et al., 2009; Vijayaraghavan and Hemanathan, 2009), or an enzyme catalyst (Li et al., 2007). The second method is the direct use of acid catalyst at the condition of atmospheric pressure and ambient temperature (Ehimen et al., 2010; Johnson and Wen, 2009; Wahlen et al., 2011). The third method involved a one-step conversion which operates at high pressure and temperature in the absence of catalyst (Huang et al., 2011; Patil et al., 2011). Benefits of using algae as one of the feedstock are due to higher photosynthethic efficiency, no sulphur in algae, non-toxic and highly biodegradable. The disadvantages using algae is due to the algae itself to produces unstable biodiesel with too many polyunsaturated, it performance is very low, and nearly to the new technology.

2.4 Esterification

Esterification is a chemical reaction which free fatty acid (FFA) reacts with alcohol to with the aid of acid catalyst form ester and water. The reaction mechanism is shown in Figure 2-1. There are two types of catalyst which are homogeneous or heterogeneous catalyst. Examples of homogeneous acids catalyst used in the esterification are sulphuric acid, phosphoric acid, organic sulfonic acids and hydrochloric acid. Homogeneous catalyst is able to reduce the time production of the biodiesel (Borges and Díaz, 2012). However, homogeneous catalyst increasing the biodiesel cost production (Domingues et al., 2013). Moreover, homogeneous acid catalyst is slower than homogeneous base catalyst reaction (Vyas et al., 2010). Heterogeneous acid catalyst is much more easily to separate from the reaction product and saponification can be avoided. Boffito et al. (2013) investigate on the esterification of FFA using a mixture of WCO, rapeseed oil as a feedstock. They found that the blending process

improve the performance of the reaction and simultaneously decreased the FFA contents in the feedstock. Abidin et al. (2012) investigated the esterification of free fatty acids in used cooking oil (UCO) using ion-exchange resins as catalysts. They achieved the FFA conversion of 92 % at the optimal condition of 60 °C for reaction temperature, 6:1 methanol to UCO molar ratio, 1.25 % w/w catalyst loading and at 475 rpm stirring. The esterification of the stearic acid using Aminophosphonic acid resin D418 was investigated by Chen et al. (2012). The research results suggested that D418 is catalytically active for the esterification of stearic acid with the conversion value of 91.47%. Furthermore, Zhang et al. (2012) study on the kinetics esterification of acidified oil using various alcohols which are butanol, propanol, methanol and ethanol. They found that butanol achieved highest FFA among others with 95.28% conversion. This is because of the properties of butanol has better miscibility than other alcohol. Su et al. (2012) investigated the catalytic performance of different homogeneous acid catalyst for the esterification of FFA and methanol. The type of catalyst used is hydrochloric acid, sulphuric and nitric acids for the esterification of FFA with methanol. From the study showed that hydrochloric achieved high yield and recoverable.

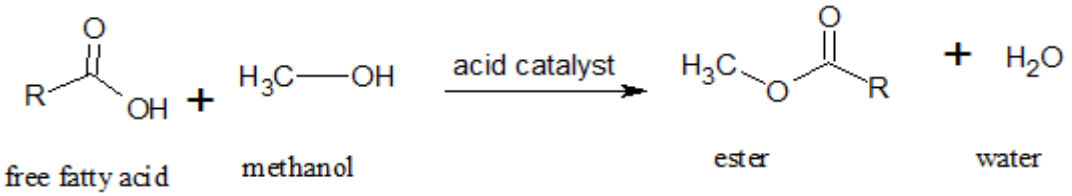

Figure 2-1: Reaction scheme for esterification process.

Table 2-1: The comparison between different type of oil and the conversion obtained.

Author	Year	Feedstock	Condition	Type Of Catalyst	Conversion
Dokic et al.	2012	Sunflower oil	Time: 4h Catalyst amount: 8.1wt% Temperature: 65 0C Oil To Methanol Ratio : 10:1	Ferric sulpfated supported on silica($Fe_2(SO_4)_3$/ Si_2O)	97.00%
Gan et al.	2012	Waste cooking oil	Catalyst amount: 4 wt% Temperature: 65 ^{0}C Oil To Methanol Ratio : 1:15	Ion exchange resin	60.20%
Guo et al.	2012	Acidified soybean soapstock	Time: 5h Temperature: 70 ^{0} C Oil To Methanol Ratio : 1:9	Lignin-derived carbanaceous	97.00%
Jeenpadiphat and Tungasmita.	2013	Palm oil	Time: 12h Temperature: 60 ^{0} C Catalyst amount: 10wt% Oil To Methanol Ratio :1:23	Acid-activated bentonite catalysts	99.00%
Shah et al.	2013	Acid Oil	Time: 8h Temperature: 100^{0}C Oil To Methanol Ratio : 1:15	Sulfonic Acid Functionalized Silica(Sio_2-Pr-SO_3H)	96.78%
Vasanthakumar and Jaharajreh.	2013	Waste cooking oil	Catalyst amount: 2 wt% Temperature: 60^{0}C Oil To Methanol Ratio : 1:9	Sulphuric acid activated biomass	85.00%
Xie et al.	2013	Vegetable oil	Time: 5h Catalyst amount: 7wt% Temperature: 67 ^{0}C Oil To Methanol Ratio : 1:15	Functionalized SBA-15 Silica	96.70%
Zhang et al.	2014	Oleic acid	Time: 12h Temperature: 100 ^{0} C Catalyst amount:3wt% Oleic acid To Methanol Ratio : 8	Sulfuric acid modified zirconia (H_2SO_4–ZrO_2)	100.00%
Ong et al.	2014	Rubber seed oil	Time: 6h Temperature: 65 ^{0} C Catalyst amount: 8wt% Oil To Methanol Ratio :1:10	Carbon supported copper oxide (CuO/C)	95.00%

2.5 Transesterification

Transesterification is a chemical reaction between glycerides, alcohol and with the aid of catalyst to produce fatty acid alkyl ester and glycerol as shown in Figure 2-2. Transesterification consist of three consecutive steps and categorized as a reversible reactions. The first reaction is triglycerides are converts to form diglycerides. Then diglycerides are changes to monoglycerides then continuous into form glycerides. Transestesterification process concerned by the reaction condition, molar ratio of alcohol to oil, type of alcohol, type and amount of catalyst used, reaction time, temperature and purity of the reactant. The advantages of alkaline catalyst are reduction of the reaction time, utilizing low temperature and decreased the cost of catalyst as compared with acid catalytic route (Gan et al., 2009). The disadvantages of transesterification process are the catalysts are difficult to separate, formation of soap, and reduction the yield of biodiesel (Cardoso et al., 2008: Haas et al., 2005). Further more, Awad et al. (2014) studied on the different types of alcohol which are methanol and ethanol in the tranesterification of waste cooking oil with the aid of alkali catalyst. They suggest that to used methanol in alkali catalyst with high content of FFA to avoid negative effect like formation of soap.

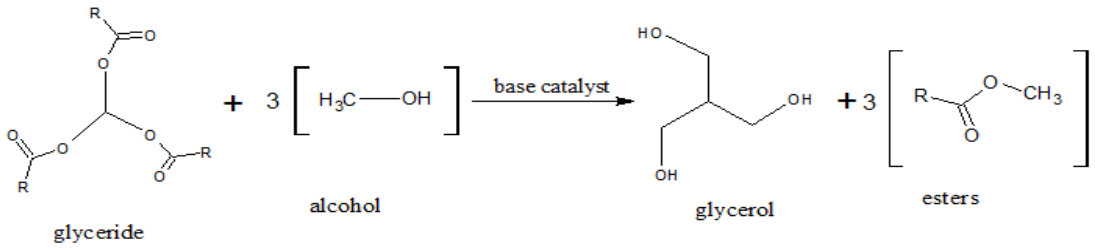

Figure 2-2: Reaction scheme for transesterification process.

2.6 Esterification- Transesterification

Esterification–transesterification is the process of the combination between two processes which is acid and based catalyzed reaction. The pre-treatment of the esterification process is conducted due to the high content of free fatty acid in raw materials. The researchers (Lu et al., 2008) have conducted two step esterification and transesterification using sulphuric acid as solid acid catalyst. Bouaid et al. (2012) has studied the optimization of a two-step process for biodiesel production from Jatropha curcas crude oil. They found that jatropha curcas crude oil can obtain higher conversion FFA. Other type of feedstock content of high FFA is Karanja oil using zeolites as a catalyst to reduce the FFA which enhances the process by two step pre-treatment (Thiruvengadaravi et al., 2012). Liu et al. (2009) studied on the esterification of rapeseed oil deodorizer distillate (RDOD) in a column reactor with cation exchange resin as catalyst. They achieved about 97.4% yield of biodiesel at the optimum condition of oil to methanol molar ratio 1:9, reaction temperature 60 °C and time is 4 h. El-Mashad et al. (2008) studied on two step process for biodiesel production from salmon oil. One-step alkaline-catalysed transesterification was found to be ineffective for biodiesel production from salmon oils because of the high acid value of the oils content. The advantage of esterification-transesterification are it requires lower reaction temperature and time duration. However, the two steps pre-treatment are difficult to obtain back the acid catalyst, corrosiveness of sulfuric acid, and high cost of equipment required for the reaction system. These processes will lead to high production cost due to large energy consumption to the separation of the catalysts from the products (Dawodu et al., 2014: Hara, 2010).

2.7 Catalyst

In biodiesel production there are usually used two types of acid catalyst which are homogeneous and heterogeneous catalyst.

2.7.1 Homogeneous catalyst

Homogeneous catalyst is used in the esterification and transesterification of vegetable oil and has a same phase as the reactants which is liquid. There are categorized into two which are homogeneous base such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) and homogeneous acid like sulfuric acid and p-sulphonic acid. In order to use the homogeneous catalyst in the transesterification, the quality of plant oil used as feedstock must be controlled. This is important to reduce the amount of free fatty acids (FFA) to the trace level because FFA leads to the various problems and simultaneously increase the cost of the production. Reactions by using alkali catalysts are usually faster compared to acid catalyst (Deeba et al., 2012). Hajek et al. (2012) studied on the effect of phase separation temperature on ester yields from ethanolysis of rapeseed oil. The process is using NaOH and KOH as catalysts. The ester in the heavier glycerol losses reduce after ethanolysis of rapeseed oil with an increase in separation temperature. The higher achievement was obtains using NaOH compare to KOH catalyst. This will increased the yield of ester phase. The process using homogeneous reaction is usually faster the conversion. However, homogeneous catalysts can consume a high production costs, caused the corrosion to equipment, existence of side reactions, generation of a substantial amount of wastewater and difficulties in catalyst recovery.

2.7.2 Heterogeneous catalysts

Heterogeneous catalyst can be classified into several different categories such as ion-exchange resins, heteropolyacids, zeolites, sulphated metal oxides and ionic liquid.

2.7.2.1 Ion exchange resin

Ion-exchange resins are more famous nowadays because they can catalyze the reaction using mild conditions due to the high concentration of acid sites (Abidin et al., 2012). Ion exchange resin normally has two ions which are cation and anion. Anion exchange rein normally is used for the basic catalyzed transesterification meanwhile cation exchange resin was used for acid catalyzed esterification (Su et al., 2010). The FFA esterification of WCO using ion exchange resins as catalyst in slurry reactor was found to be convenient and easy-to handle process to lower acidity (Boffito et al., 2013).

(Haigh et al., (2013) studied the esterification reaction using two types of catalysts which are ion exchange resin (Purolite D5081) and immobilised enzyme (Novozyme 435). It shows that a FFA conversion of 94% was achieved using Purolite D5081 and Novozyme 435 resulted in 90% conversion. In addition, it has been found that with Novozyme 435 lead to side reactions such as the formation of additional fatty acid methyl esters (FAMEs) and FFAs at longer reaction times. Feng et al. (2010) also studied on the biodiesel production using different type of cation exchange resin which is NKC-9, 001×7, and D61. They found that NKC-9 obtain higher conversion compared to others because of its high catalytic activity.

2.7.2.2 Heteropoly acids

Heteropoly acids are typical strong Bronsted acids. It is an eco-friendly insoluble solid acid catalyst which has a high thermal stability and surface area by supporting them on suitable support thus increased the catalytic activity. The FFA esterification using 12-tungstophosphoric acid (TPA) supported on niobia Nb_2O_5 was studied by (Srilatha et al., 2009). At high calcination temperature the TPA is able to reduce into its metal oxides which reduce the acidity of the catalyst.

2.7.2.3 Zeolite

Zeolites are defined as the microporous crystalline solids. Zeolites can be synthesized with several of acidic and textural properties to overcome the diffusional limitations (Helwani et al., 2009). Thiruvengadaravi et al., (2012) studied on the esterification of pongamia pinnata oil using two different types of zeolites which are H-ZSM 5 and H-Y. They found that H-Y shows to be more effective in the conversion of FFA. This is because FFA can be reduce using H-Y is less compared to H-ZSM. Baroi et al., (2014) studied on biofuel production from green seed oil using zeolites which involve with esterification and transesterification process. The tungsten oxide (WO_3) and TPA was supported on three different type of zeolites catalyst which is H-Y, H-β and H-ZSM-5. H-Y zeolite showed higher catalytic activity for esterification otherwise H-β zeolite for the transesterification reaction compared to other catalysts. A 55% of TPA/H-β obtains optimum catalytic activity for both processes. This shows that H-β to be an efficient catalyst to produce high quality biodiesel from green seed canola oil.

2.7.2.4 Sulphated metal oxides

Sulfated metal oxides are a group of strong acid catalysts. Sulfated zirconia catalyst shows the highest catalytic activity and 85% of FFA conversion (Deshmane and Adewuyi, 2013). Konwar et al., (2014) studied on the biodiesel production from acid oils using sulfonated carbon catalyst. Sulfonated carbon catalyst was reduce the FFA to level below 2 wt% and obtain about 71% conversion with acid oil contain of 43.7%. This is because sulfonated carbons exhibit high acid exchange capacity, excellent thermal stability and reusability.

2.7.2.5 Ionic liquid

IL is a group of salt with a wide range of temperature range for the liquid phase. It consists of large organic cations such as ammonium, imidazolium and pyridinium. IL can be categories into water miscible (hydrophilic) and water immiscible (hydrophobic). Liang, (2013) studied using solid acidic ionic liquid polymer as a catalyst for biodiesel synthesis using waste oil and achieved the yield about 99%. Man et al., (2013) studied the esterification of FFA using a bronsted ammonium ionic liquid as the catalyst in the first pre treatment of crude palm oil (CPO). They found that conversion rate of FFA achieved 82.1% when 5.2 wt% of triethylammonium hydrogensulfate (Et_3NHSO_4) was used for the reaction of methanol with CPO at a ratio of 15:1 and reaction temperature of 170 ◦C for 3 h. Typically, the acidic ionic liquid gives some back draws such as solubility with some organic compound, catalyst loss during the process, and difficulties to purify back the catalyst. The immobilization of ionic liquids became a good choice to overcome those problems such as using silica, porous silica and polystyrene. Qiao et al. (2006) studied on the acidic ionic liquid in modified silica gel as the catalyst for esterification. They found that modified silica gel can behave as recyclable solid catalyst because it was form by covalent bond. The disadvantages of using silica, polystyrene and porous silica are high cost, toxic and expensive. Divinyl benzene (DVB) shows good properties such as reduce the cost because does not use expensive reagent. The ionic liquid were attached to the surface of Poly DVB sphere with covalent bonds to made active sites accessible easily and reduced the mass transfer resistance (Liang, 2013).

3 MATERIALS AND METHODS

3.1 Materials

Methanol, 99%, isopropanol, 99%, acetonitrile, 99%, sulphuric acid, 96%, diethyl ether, 95%, sulphuric acid, 96% was purchase from Fisher. Alpha- naphtholbenzein indicator grade, potassium hydroxide solution in 0.1M of KOH in isopropanol, 99%, oleic acid, 99% and azobisisobutyronitrile, 99% are purchased from Sigma Aldrich and trimethyl-1-pentene, 99%, divinyl benzene, 99% was supplied by Fluka (Steinheim, Germany).

3.2 Characterization of catalyst

The characterizations of the triethylammonium hydrogen sulphate ionic liquid catalyst are using Fourier Transform Infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), Brunauer- Emmett- Teller (BET) and Nuclear Magnetic Resonance (NMR).

3.2.1 Fourier Transform Infrared spectroscopy (FTIR)

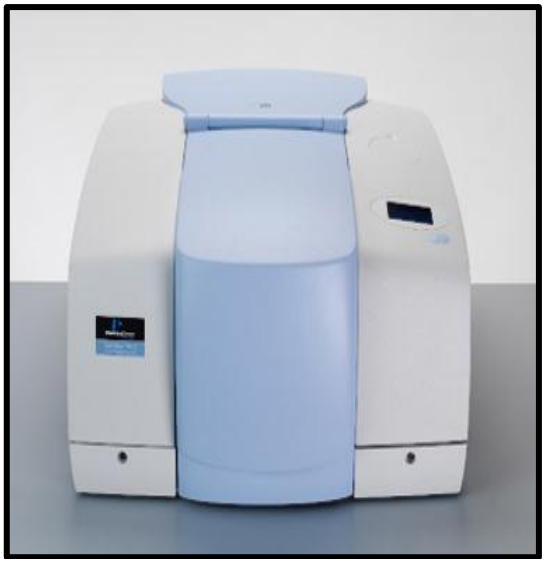

Figure 3-1: FTIR machine model Spectrum 1000

Fourier Transform Infrared spectroscopy (FTIR) was used to determine the functional group of chemical presence in the sample. The FTIR spectrum was obtain using with Spectrum 1000 liquid pool as shown in

Figure 3-1. The sample was drop at KBr disk. The second disk was placed on first disk to spread the liquid in a thin layer. Then, the disk was clamped together. The IR